

1,5-MIGRATIONS OF SILICON BETWEEN OXYGEN CENTERS IN SILYL β -DIKETONES

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Summary

A series of acyclic silyl diketonates, $(\text{CH}_3)_3\text{Si}(\text{dik})$, where dik = dipivaloylmethanate, diisobutyrylmethanate and hexafluoroacetylacetonate, along with a new series of cyclic acetylacetonates of the type $\text{CH}_3(-\text{CH}_2(\text{CH}_2)_x\text{CH}_2-)\text{Si}(\text{acac})$, where $x = 1, 2, \text{ and } 3$, have been shown to possess enol ether structures in which the acyl group is positioned *cis* or *trans* to the silyl group. The ratios of *cis* to *trans* configurations in the $(\text{CH}_3)_3\text{Si}(\text{dik})$ series increase from <0.02 to >50.0 in the order of diketonate substituents $\text{CF}_3 < \text{CH}_3 < i\text{-C}_3\text{H}_7 < t\text{-C}_4\text{H}_9$. The ratios for the $\text{CH}_3(-\text{CH}_2(\text{CH}_2)_x\text{CH}_2-)\text{Si}(\text{acac})$ compounds increases in the order $x = 1 > 2 > 3$. These data are interpreted in terms of incipient pentacoordination of silicon by the carbonyl oxygen atom in the *cis* isomer. Rates of 1,5-migration of silicon between oxygen centers in the *cis* isomers have been determined by NMR spectroscopy. The dependence of the rearrangement rates on diketonate substituent and angle strain at silicon indicate that the migration process is better viewed as an internal nucleophilic displacement, rather than a sigmatropic shift. 1,5-Migration in the chiral $(\text{C}_6\text{H}_5\text{CH}_2)(\text{CH}_3)(\text{C}_6\text{H}_5)\text{Si}$ derivative of dipivaloylmethanate occurs exclusively with retention of configuration at silicon. The large difference in activation energy for migration and inversion (>18 kcal/mol) precludes the possibility of distinguishing between a stepwise and concerted displacement mechanism.

Introduction

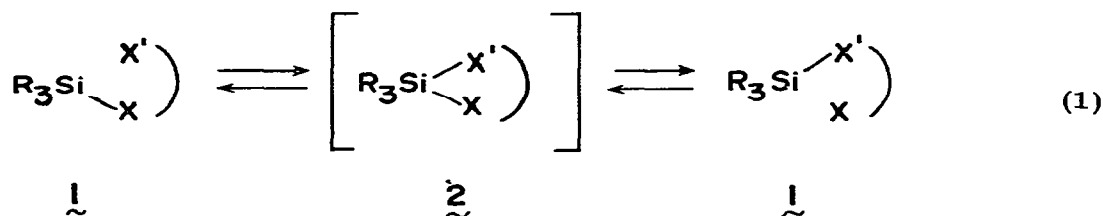
Most nucleophilic displacement reactions of organosilicon compounds of the type R_3SiX have been described by Sommer [1] as occurring by means of an $\text{S}_{\text{N}}2\text{-Si}$ or $\text{S}_{\text{N}}\text{i-Si}$ mechanism. The former mechanism results in inversion of con-

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figuration at silicon, whereas the latter leads to retention. Both are believed to be concerted processes, or, if not concerted, involve at best the formation of an unstable intermediate. Although Sommer has maintained that displacements occurring via an authentic pentacoordinated intermediate containing five full bonds to silicon (designated S_N2^* -Si or S_N2^{**} -Si) are rare, others have suggested [2] that several, especially those occurring with retention, may proceed by an addition-elimination mechanism in which a trigonal bipyramid capable of pseudorotation is formed along the reaction coordinate. Mislow [3] has already pointed out, however, that the evidence in favor of such processes in silicon chemistry is considerably less compelling than that which exists for the mechanism of displacement reactions of tetrahedral phosphorus compounds.

One class of compounds that is potentially useful in probing the mechanisms of displacement reactions of organosilicon possesses structures which may be represented schematically by 1, wherein X—X' in its unsilylated form is a symmetric and uninegative ligand and X is an electronegative atom such as oxygen or nitrogen.

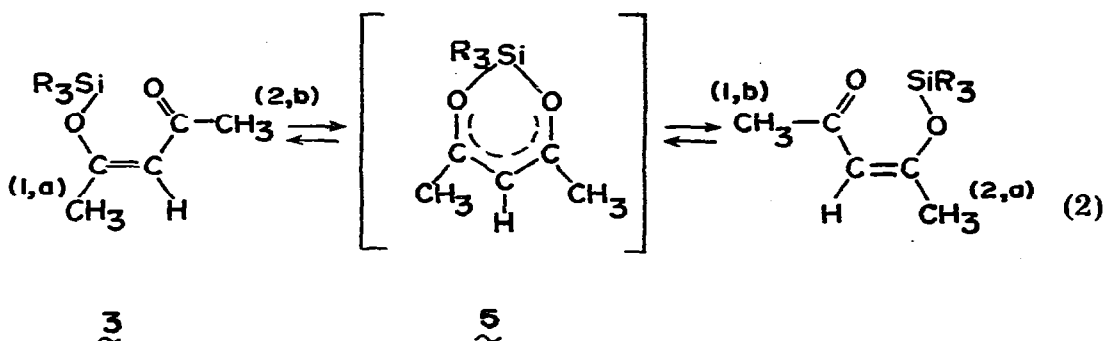
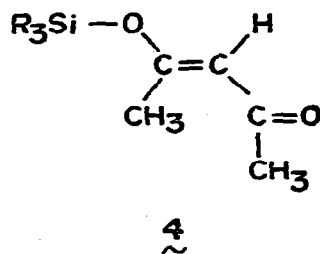
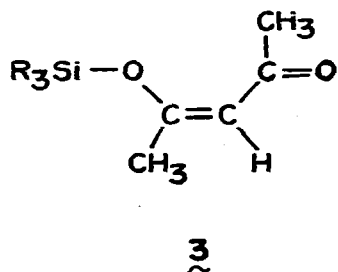


Because of the symmetric nature of the ligand linking X and X', these compounds are usually structurally non-rigid and undergo a rapid, intramolecular degenerate rearrangement illustrated by equation 1. Examples include silyl derivatives of β -diketones [4–8], malonates [9], tropolone [7], pyrazoles [10], triazene [11], benzamidine [12], and hydrazine anions [13]. The degenerate rearrangements in most cases are presumed to proceed by front-side nucleophilic attack at silicon to give a cyclic transition state or intermediate 2 much like the mode of activation for bimolecular displacement reactions that occur with retention. When X and X' represent different electronegative atoms, as in silyl anilides [14,15] and amides [16], then X- and X'-silylated diastereomers are possible, and a similar intramolecular process leads to their rapid isomerization. These so-called silatropic shifts can play an important role in the use of silyl derivatives in regiospecific synthesis [17].

In the present study a new series of silyl diketonates have been prepared and investigated by NMR spectroscopy in an attempt to evaluate the relative merit of a concerted versus an addition-elimination mechanism for their degenerate rearrangements. Acyclic silyl acetylacetonates, $\text{R}_3\text{Si}(\text{acac})$, have been previously shown to possess open-chain enol ether structures [4–8] in which the acyl group is *cis* (3) or *trans* (4) to the silyl group.

The *cis* isomer undergoes the 1,5-silatropic shift of interest (eq. 2), whereas the *trans* isomer is stereochemically inert. It has also been shown that the 1,5-shift of the *cis* isomer occurs with retention of configuration at silicon [7,8].

The objective of the present work is to more firmly establish that the degenerate rearrangements of the *cis* isomer are best viewed as internal nucleophilic

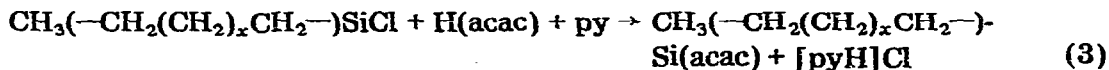


displacement processes (rather than, say, sigmatropic shifts) by examining the effects of (1) angle strain at silicon and (2) alkyl group substitution at the diketone on the rates of rearrangement. Also, a new asymmetric silyl β -diketonate derivative has been prepared in an attempt to observe intramolecular inversion at silicon under conditions where the 1,5-silatropic shift is fast. The occurrence of intramolecular inversion would prove that an authentic penta-coordinate intermediate capable of pseudorotation is formed in the internal nucleophilic displacement process.

Results and discussion

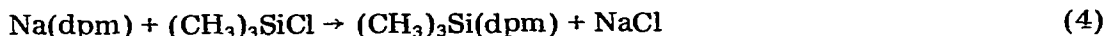
Preparation and characterization of compounds

To obtain a series of silyl β -diketonates with differing angle strain at silicon, silacycloalkane acetylacetonate derivatives of the type $\text{CH}_3(-\text{CH}_2(\text{CH}_2)_x\text{CH}_2-)\text{Si}(\text{acac})$, where $x = 1, 2, \text{ or } 3$, were prepared by reaction of the appropriate chlorosilane with acetylacetonate in the presence of pyridine (eq. 3).

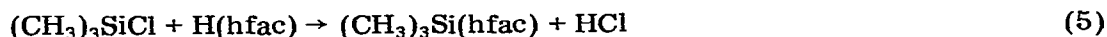


Equation 3 is also useful for the synthesis of acyclic silyl derivatives of acetylacetonate, such as $(\text{CH}_3)_3\text{Si}(\text{acac})$ [18]. However, with less acidic diketones containing more electron releasing alkyl substituents, as in dipivaloylmethane, $\text{H}(\text{dpm}) = (\text{t-C}_4\text{H}_9)\text{COCH}_2\text{CO}(\text{t-C}_4\text{H}_9)$, or diisobutyrylmethane, $\text{H}(\text{dibm}) = (\text{i-C}_3\text{H}_7)\text{COCH}_2\text{CO}(\text{i-C}_3\text{H}_7)$, no reaction is observed with $(\text{CH}_3)_3\text{SiCl}$ in the presence of pyridine. On the other hand, with strongly acidic hexafluoroacetylacetonate, $\text{H}(\text{hfac}) = \text{CF}_3\text{COCH}_2\text{COCF}_3$, the reaction mixture yields only pyridinium hexafluoroacetylacetonate.

Therefore, trimethylsilyl derivatives of H(dpm) and H(dibm) were prepared by reaction in ether of their sodium salts with $(\text{CH}_3)_3\text{SiCl}$ [19]:



$(\text{CH}_3)_3\text{Si(hfac)}$ was prepared by reaction of the free diketone with excess $(\text{CH}_3)_3\text{SiCl}$ [19]:



A racemic mixture of $(\text{CH}_3)(\text{C}_6\text{H}_5)(\text{C}_6\text{H}_5\text{CH}_2)\text{Si(dpm)}$ was obtained from the corresponding chlorosilane and Na(dpm). This compound is ideally suited for estimating rates of inversion at silicon because it exists almost exclusively as the *cis* isomer, and the diastereotopic benzyl protons give rise to an AB NMR pattern ($\delta = 11.0$ ppm, $J = 13.5$ Hz) under conditions where the 1,5 silyl group migration is fast (vide infra).

All of the silyl β -diketones prepared in this study adopt enol ether structure analogous to $(\text{CH}_3)_3\text{Si(acac)}$ [18–20], as judged by IR and NMR spectroscopy. Each compound exhibits an uncoordinated C=O stretching vibration in the region 1659–1733 cm^{-1} . The C=C stretch is found in the region 1588–1625 cm^{-1} and the Si–O stretch ranges from 945 cm^{-1} for $(\text{CH}_3)_3\text{SiHfac}$ to 1100 cm^{-1} for $(\text{CH}_3)_3\text{Si(dpm)}$. With the exception of $(\text{CH}_3)_3\text{Si(hfac)}$, the *cis* isomers give rise to time-averaged enol ether methyl proton resonances due to rapid 1,5 internal migration of the silyl group. The *trans* isomers, where observed, are stereochemically inert, because of the high barrier to rotation about the localized C=C bond. $(\text{CH}_3)_3\text{Si(hfac)}$ exists almost exclusively as the *trans* isomer as indicated by the presence of two lines of equal intensity in the ^{19}F NMR spectrum ($\delta = 4.65$ ppm).

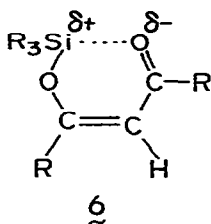
Cis to *trans* isomer ratios for the new silyl enol ethers, along with the value determined previously for $(\text{CH}_3)_3\text{Si(acac)}$, are given in Table 1. Among the $(\text{CH}_3)_3\text{Si}$ derivatives of acac, dibm, and dpm, the percent *cis* isomer present at equilibrium is 25%, 35%, and >98%, respectively. It is likely that the increasing steric requirements of the diketone substituent in this series tends to favor the *cis* isomer over the *trans* isomer (cf., conformations illustrated by 3 and 4). However, with $(\text{CH}_3)_3\text{Si(hfac)}$, where the steric requirements of the terminal

TABLE 1
EQUILIBRIUM ISOMER RATIOS AT 25°C FOR SILYL β -DIKETONES ^a

Compound	Diketone substituent	[<i>cis</i>]/[<i>trans</i>]
$\text{CH}_3(-\text{CH}_2(\text{CH}_2)\text{CH}_2-)\text{Si(acac)}$	CH_3	2.23
$\text{CH}_3(-\text{CH}_2(\text{CH}_2)_2\text{CH}_2-)\text{Si(acac)}$	CH_3	0.45
$\text{CH}_3(-\text{CH}_2(\text{CH}_2)_3\text{CH}_2-)\text{Si(acac)}$	CH_3	0.25
$(\text{CH}_3)_3\text{Si(acac)}$ ^b	CH_3	0.34
$(\text{CH}_3)_3\text{Si(dibm)}$	$\text{CH}(\text{CH}_3)_2$	0.55
$(\text{CH}_3)_3\text{Si(dpm)}$	$\text{C}(\text{CH}_3)_3$	>50
$(\text{CH}_3)(\text{C}_6\text{H}_5)(\text{C}_6\text{H}_5\text{CH}_2)\text{Si(dpm)}$	$\text{C}(\text{CH}_3)_3$	>50
$(\text{CH}_3)_3\text{Si(hfac)}$	CF_3	<0.02

^a The ratios were determined in CCl_4 at a concentration of 25 ml/100 ml of solvent. ^b The value for this compound was taken from ref. 5; the solvent is chlorobenzene; concentration is 0.6 M.

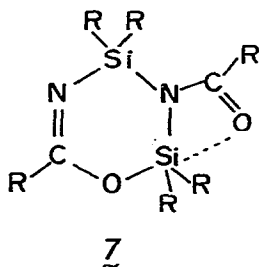
CF_3 groups are comparable to those of the methyl groups in acetylacetone, the *cis* isomer is unobserved (<2%). This suggests that inductive effects of the diketone substituents are also important in determining the stability of the *cis* isomer. The inductive effects may be operating by way of a long range electrostatic interaction between silicon and the acyl oxygen in the *cis* isomer; as illustrated by structure 6. The extent of this interaction would be considerably reduced when a good electron releasing group ($\text{R} = \text{CH}_3$, $i\text{-C}_3\text{H}_7$, or $t\text{-C}_4\text{H}_9$) is replaced by an electron withdrawing group ($\text{R} = \text{CF}_3$).



The *cis* to *trans* ratio of $\text{CH}_3(-\text{CH}_2\text{CH}_2\text{CH}_2-)\text{Si}(\text{acac})$ is five to nine times larger than the values observed for the corresponding silacyclopentane and silacyclohexane derivatives. This range in values for the silacycloalkane derivatives is much larger than expected based on differences in the inductive effects of substituents on silicon [5]. Since the long range interaction proposed for the acyclic derivatives is expected to occur via a tetrahedral face of silicon, angle strain at silicon in the silacyclobutane derivative should enhance the stability of the *cis* isomer relative to the *trans* isomer.

Although the variation in *cis* to *trans* ratios among the silyl β -diketones in this study can be explained by an incipient pentacoordinate interaction, we must point out that physical verification of the interaction is lacking. A long range interaction between silicon and the acyl oxygen in the *cis* isomer may be expected to shift the carbonyl frequency to lower energy, relative to the *trans* isomer. However, the IR results are equivocal. Both $(\text{CH}_3)_3\text{Si}(\text{acac})$ and $\text{CH}_3(-\text{CH}_2\text{CH}_2\text{CH}_2-)\text{Si}(\text{acac})$ exhibit two bands in the carbonyl region near 1678 and 1660 cm^{-1} , and the lower energy band can be reasonably assigned to the *cis* isomer. On the other hand, $\text{CH}_3(-\text{CH}_2(\text{CH}_2)_2\text{CH}_2-)\text{Si}(\text{acac})$ and $\text{CH}_3(-\text{CH}_2(\text{CH}_2)_3\text{CH}_2-)\text{Si}(\text{acac})$ exhibit one $\text{C}=\text{O}$ band near 1679 cm^{-1} , suggesting that the carbonyl frequencies for the *cis* and *trans* isomers are nearly the same.

Direct evidence for intramolecular incipient extracoordination of silicon has been observed previously [21] for a disiloxadiazine, 7, in which the $\text{Si}-\text{O}$ distance (2.61 \AA) is 0.74 \AA less than the sum of the respective Van der Waals radii but well outside the range expected for an authentic covalent bond ($1.61-1.81 \text{ \AA}$).



An X-ray crystallographic structure determination of a solid phase *cis*-silyl β -diketone would be of interest.

Migration kinetics

First-order rate constants for the internal 2,5-migration of silicon between oxygen centers in the *cis* silyl β -diketones were determined from the simplified Gutowsky-Holm NMR equation for chemical exchange of nuclei between two equally populated environments [22], where k_c is the first-order rate constant

$$k_c = (\pi/\sqrt{2})\Delta\nu_0 \quad (6)$$

(sec^{-1}) for exchange at the coalescence temperature (T_c) and $\Delta\nu_0$ is the frequency separation (Hz) between the resonance positions of the nuclei at the coalescence temperature in absence of chemical exchange.

Fig. 1 illustrates the diketone methyl and silyl methyl resonance lines of a

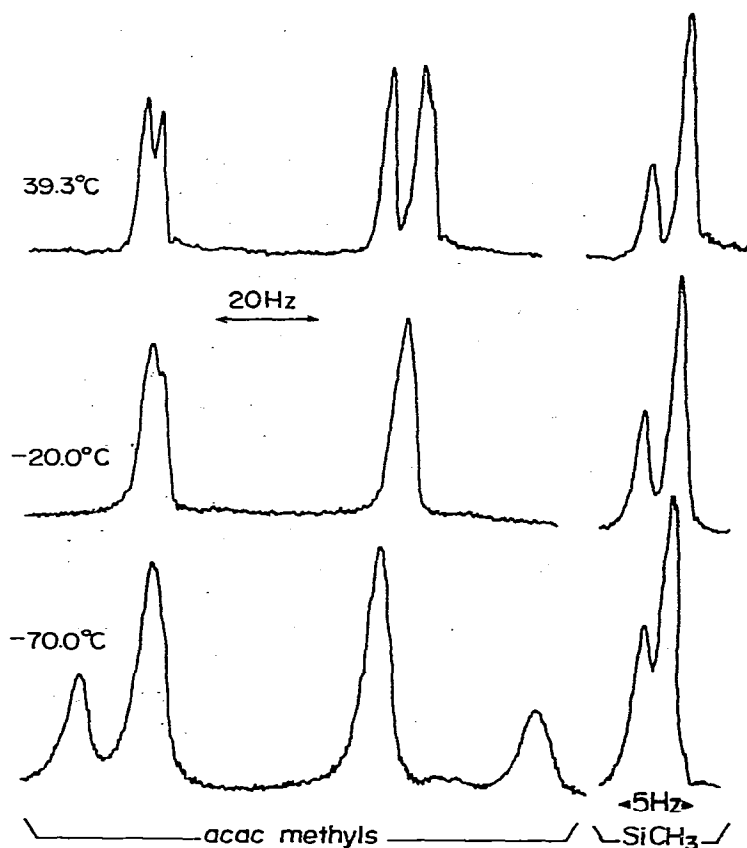


Fig. 1. Acetylacetonate and silyl methyl proton resonance lines for a *cis/trans* mixture of $\text{CH}_3(\text{CH}_2)_3\text{CH}_2\text{Si}(\text{acac})$ in CH_2Cl_2 . The highest and lowest field diketone methyl lines in the slow exchange region (-70.0°C) belong to the *cis* isomer. At the coalescence temperature (-20°C) the time averaged *cis* line is so broad that it is barely discernible above the spectral background. The time averaged *cis* line in the fast exchange region (39.3°) appears as the second highest field line in the acetylacetonate methyl region. The small splitting of the *trans* methyl lines arises from coupling to the $=\text{CH}$ -proton of the diketone.

cis-trans mixture of $\text{CH}_3(-\text{CH}_2(\text{CH}_2)_3\text{CH}_2-)\text{Si}(\text{acac})$ at the coalescence temperature for the *cis* isomer (-20°C) and at temperatures where the 1,5-migration is slow (-70°C) and fast (39.3°C). Similar spectra were obtained for $\text{CH}_3(-\text{CH}_2(\text{CH}_2)_2\text{CH}_2-)\text{Si}(\text{acac})$. However, only time averaged spectra were obtained for the *cis* isomers of $(\text{CH}_3)(-\text{CH}_2\text{CH}_2\text{CH}_2-)\text{Si}(\text{acac})$ and $(\text{CH}_3)_3\text{Si}(\text{dpm})$ even at the lowest temperatures accessible to us ($\sim -140^\circ\text{C}$). Also, the coalescence temperature of *cis*- $(\text{CH}_3)_3\text{Si}(\text{dibm})$ could not be determined because of limited solubility and line overlap by the resonances of the *trans* isomer. Therefore, only minimum rate constant values were obtained for the latter three compounds.

Table 2 provides $\Delta\nu_0$, T_c , and k_c values along with calculated values of ΔG^\ddagger at T_c and extrapolated values of the rate constant at 25°C (k_{25°). These data show that the rate of silyl group migration depends dramatically on angle strain at silicon. The difference in ΔG^\ddagger between the silacyclobutane and -hexane derivatives of acetylacetonate is >6.4 kcal/mole. The migration rate is also strongly dependent on the β -diketone substituent. For example, ΔG^\ddagger for $(\text{CH}_3)_3\text{Si}(\text{acac})$ is >6.7 kcal/mole larger than ΔG^\ddagger for $(\text{CH}_3)_3\text{Si}(\text{dpm})$. The influence of diketone substituents on the rate of migration is significantly greater than that previously observed for silyl group substituents [5].

Although the coalescence temperature for $(\text{CH}_3)_3\text{Si}(\text{dpm})$ is below -137°C , the chiral analog $(\text{CH}_3)(\text{C}_6\text{H}_5)(\text{C}_6\text{H}_5\text{CH}_2)\text{Si}(\text{dpm})$ exhibits a coalescence temperature of -85°C , as shown in Fig. 2. Increasing the steric bulk at silicon increases ΔG^\ddagger for silyl group migration in dpm by >2.4 kcal/mole (cf., Table 2). The most interesting feature of the chiral derivative, however, is that the AB pattern for the diastereotopic benzyl protons on silicon is retained at temperatures where the 1,5-migration is fast. This means that the migration occurs with retention of configuration at silicon. The AB pattern is present even at 211°C in chloronaphthalene solution.

Based on estimated value of $\Delta\nu_0$ for the benzyl protons of $(\text{CH}_3)(\text{C}_6\text{H}_5)(\text{C}_6\text{H}_5\text{CH}_2)\text{Si}(\text{dpm})$ at 211°C (3.6 Hz), ΔG^\ddagger for inversion is >27 kcal/mole. The first order rate constant extrapolated to 25°C is $<2 \times 10^{-7} \text{ sec}^{-1}$. This means that fewer than one out of every 10^{13} 1,5-migrations at 25°C results in inver-

TABLE 2

NMR KINETIC DATA FOR 1,5-MIGRATION OF SILYL GROUPS IN *cis*-SILYL β -DIKETONES

Compound	Solvent	$\Delta\nu_0$ (Hz)	T_c ($^\circ\text{C}$)	K_c (sec^{-1})	ΔG^\ddagger (kcal/mole)	$k_{25^\circ\text{C}}$ (sec^{-1})
$\text{CH}_3(-\text{CH}_2\text{CH}_2\text{CH}_2-)\text{Si}(\text{acac})$	CHClF_2	17.2 ^a	< -142	>38.1	<6.5	$>1 \times 10^8$ ^d
$\text{CH}_3(-\text{CH}_2(\text{CH}_2)_2\text{CH}_2-)\text{Si}(\text{acac})$	CHClF_2	17.2	-89	38.1	9.3 ± 0.3	1×10^5
$\text{CH}_3(-\text{CH}_2(\text{CH}_2)_3\text{CH}_2-)\text{Si}(\text{acac})$	CH_2Cl_2	17.1	-20	38.1	12.9 ± 0.3	2×10^3
$(\text{CH}_3)_3\text{Si}(\text{acac})$ ^b	$\text{C}_6\text{H}_5\text{Cl}$	33.0	5.0	73.3	13.9 ± 0.4	4×10^2
$(\text{CH}_3)_3\text{Si}(\text{dibm})$	CH_2Cl_2	4.0 ^c	< -58	>8.9	<11.5	$>2 \times 10^4$
$(\text{CH}_3)_3\text{Si}(\text{dpm})$	CHClF_2	4.0 ^c	< -137	>8.9	<7.2	$>3 \times 10^7$
$(\text{CH}_3)(\text{C}_6\text{H}_5)(\text{C}_6\text{H}_5\text{CH}_2)\text{Si}(\text{dpm})$	CHClF_2	22.0	-85	48.9	9.4 ± 0.3	8×10^5

^a This value of $\Delta\nu_0$ was estimated from the values observed for the corresponding silacyclopentane and -hexane derivatives. ^b The NMR spectral data for this compound were taken from refs. 4 and 5. ^c These values were estimated from the value of $\Delta\nu_0$ observed for *trans*- $(\text{CH}_3)_3\text{Si}(\text{dibm})$. ^d Extrapolated values of the rate constant at 25°C were obtained by assuming $\Delta S^\ddagger = 0$.

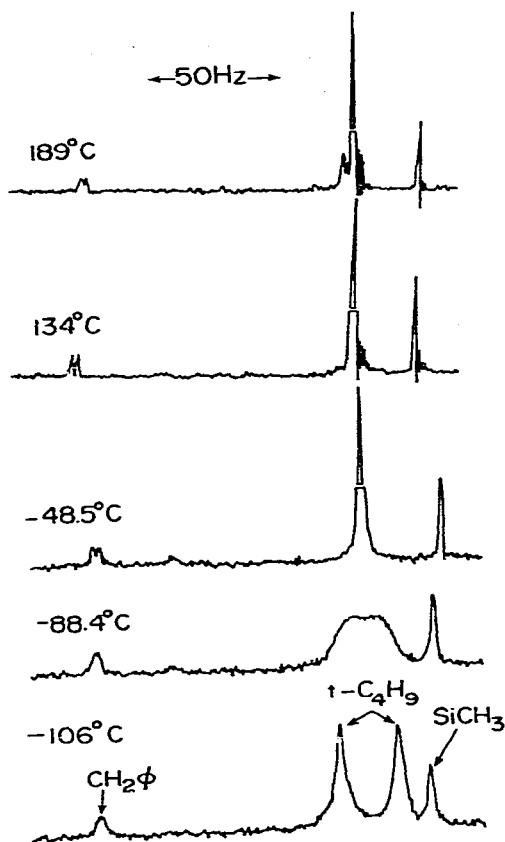


Fig. 2. Proton NMR spectra of $(\text{CH}_3)(\text{C}_6\text{H}_5)(\text{C}_6\text{H}_5\text{CH}_2)\text{Si}(\text{dpm})$. The low temperature spectra (-106 to -48.5°C) were recorded in CHClF_2 , and the high temperature spectra (134°C , 189°C) were recorded in chloronaphthalene. The AB pattern of the benzyl protons is obscured at lower temperatures because of line broadening. At the spectral amplitudes employed only the inner lines of the four-line AB pattern are observed.

sion at silicon. The minimum difference in ΔG^\ddagger for 1,5-migration and inversion pathways (>18 kcal/mole) is much larger than the value (>9.2 kcal/mole) previously determined by Reich and Murcia [7] from ^{13}C NMR studies of an $\text{R}_3\text{Si}(\text{acac})$ derivative.

Mechanistic implications

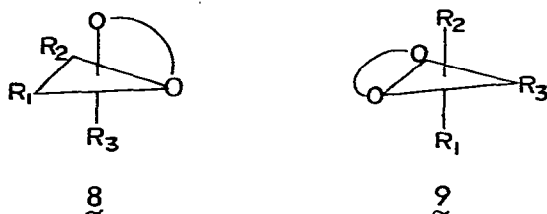
The dependence of the rates of 1,5-silyl group migration in *cis*-silyl β -diketones on angle strain at silicon and inductive effects of the diketone substituents more firmly establishes the mechanism as an internal nucleophilic displacement process involving a pentacoordinate intermediate or transition state (cf., eq. 2, 5).

As the angle strain at silicon in the $\text{CH}_3(-\text{CH}_2(\text{CH}_2)_x\text{CH}_2-)\text{Si}(\text{acac})$ series increases in the order $x = 1 < 2 < 3$, the first order rate constants increase dramatically, with the relative values at 25°C being $1 : 10^{2.7} : >10^{4.7}$. These relative values agree well with the $1 : 10^2 : \sim 10^{5.7}$ relative rates for hydrolysis of

cyclic organosilicon hydrides containing six-, five-, and four-membered rings [23].

Reich and Murcia [7] have suggested that the barriers to 1,5 migration in β -diketones are more indicative of a nucleophilic displacement than a concerted sigmatropic shift. The dependence of ΔG^\ddagger on inductive effects of the diketone substituents (e.g., the >6.7 kcal/mole difference in the barriers for *cis*-(CH₃)₃-Si(acac) and *cis*-(CH₃)₃Si(dpm)) and the silyl substituents [5] are better indicators of a displacement process. Sigmatropic shifts of silyl groups, as in the 1,3-migrations of allylsilanes [24], exhibit little or no substituent effects.

Since the 1,5-migration of *cis*-silyl β -diketones occurs with retention of configuration, the front-side attack of the acyl oxygen affords an activated species that may resemble a square pyramid with the diketone spanning a basal edge, or better, a trigonal bipyramid with the diketone spanning an axial-equatorial edge (8). Unfortunately, we were not able to observe inversion at silicon for



(CH₃)(C₅H₆)(C₆H₅CH₂)Si(dpm). Thus it is not certain whether 8 is an authentic intermediate capable of pseudorotation about the equatorial oxygen to give 9, which would be the expected intermediate in an inversion process. However, based on the differences in rates of 1,5-migration and inversion, we are able to conclude that 9 is >18 kcal/mole higher in energy than 8.

Experimental

General methods. 1-Methyl-1-chloro-1-silacyclobutane and the analogous silacyclopentane and silacyclohexane were prepared by procedures described previously [25,26]. All solvents were dried over suitable reagents and freshly distilled before use. All reactions and manipulations of hygroscopic reagents and products were carried out in a dry-nitrogen atmosphere. Liquid products were purified by fractional distillation through a 12 cm jacketed Vigreux column.

Infrared spectra were obtained using 5% (v/v) solutions in CCl₄ or CH₂Cl₂ and 0.1 mm path length KBr cells. Values of $\Delta\nu_0$ for use in the Gutowsky-Holm equation were obtained, where possible, by linear extrapolation of the temperature dependence of the frequency separation in the region of slow exchange. Coalescence temperatures were checked at different concentrations to ensure that the 1,5-migrations occurred by a first-order process. Values of ΔG^\ddagger were calculated from transition state theory. Errors in ΔG^\ddagger were estimated from the uncertainties in the coalescence temperatures. Extrapolated values of first-order rate constants were calculated by assuming $\Delta S^\ddagger = 0$. The activation entropy for 1,5-silyl group migration in *cis*-(CH₃)₃Si(acac) has been previously shown to be zero within experimental error [5]. Equilibrium *cis/trans* ratios were deter-

mined by planimetric integration of $-\text{CH}=\text{}$ resonances. Up to two weeks was allowed for equilibrium to be established at 25°C .

Trimethylsilylhexafluoroacetylacetone. A mixture of 11.7 g (0.0560 mol) of hexafluoroacetylacetone and 20.0 ml (0.157 mol) of trimethylchlorosilane was heated at reflux temperature for eleven days. The reaction mixture was distilled under dry-nitrogen at atmospheric pressure to give trimethylsilylhexafluoroacetylacetone in 43% yield (b.p. $128\text{--}129^\circ\text{C}$).

Anal. Found: C, 34.9; H, 4.01; F, 40.6; Si, 10.9. $\text{C}_8\text{H}_{10}\text{F}_6\text{O}_2\text{Si}$ calcd.: C, 36.0, H, 3.57; F, 40.7; Si, 10.0%.

Trimethylsilyldipivaloylmethane. The sodium salt of dipivaloylmethane was prepared by reaction of stoichiometric amounts of the diketone and sodamide or sodium metal in diethyl ether at room temperature. A solution of the salt (0.40 g, 0.05 mol) in 50 ml of ether was added slowly to a solution of 5.9 g (0.054 mol) of trimethylchlorosilane in 50 ml of ether. Distillation of the mixture under reduced pressure gave a colorless product (b.p. $44\text{--}45^\circ\text{C}$, 0.04 Torr).

Anal. Found: C, 66.2; H, 11.2; Si, 11.6. $\text{C}_{14}\text{H}_{28}\text{O}_2\text{Si}$ calcd.: C, 65.6; H, 11.0; Si, 11.0%.

Trimethylsilyldiisobutyrylmethane. This compound was prepared in 50% yield by a method analogous to that described above for the dipivaloylmethane analog (b.p. $55\text{--}58^\circ\text{C}$, 0.1 Torr).

Anal. Found: C, 63.3; H, 10.7. $\text{C}_{12}\text{H}_{24}\text{O}_2\text{Si}$ calcd.: C, 63.1; H, 10.6%.

Benzylmethylphenylsilyldipivaloylmethane. The synthetic procedure was analogous to that described for trimethylsilyldipivaloylmethane. Distillation of the product under reduced pressure gave a viscous pale yellow product (b.p. $183\text{--}185^\circ\text{C}$; 0.1 Torr). The yield was 51%.

Anal. Found: C, 76.34; H, 8.60; Si, 7.05. $\text{C}_{25}\text{H}_{34}\text{O}_2\text{Si}$ calcd.: C, 76.09; H, 8.68; Si, 7.12%.

Silacycloalkane Acetylacetonates. All of the silacycloalkane derivatives of acetylacetone were prepared in 22 to 25% yield by the following general procedure. A solution of pyridine (ca., 0.1 mol) in hexane (ca., 20 ml) was added slowly to equimolar amounts (ca., 0.1 mol) of acetylacetone and the silane in hexane (ca., 80 ml). The mixture was allowed to stir at room temperature overnight, except in the reaction with the silacyclobutane, in which case the mixture was stirred for one hour. The pyridinium chloride was removed by filtration, and the hexane was removed under vacuum. The remaining liquid residue was filtered again and distilled under reduced pressure. The silacyclobutane derivative was stored at -78°C to slow its decomposition via ring opening [27].

$\text{CH}_3(-\text{CH}_2\text{CH}_2\text{CH}_2-)\text{Si}(\text{acac})$: b.p. $37\text{--}38^\circ\text{C}$ (0.2 Torr). Anal. Found: C, 58.63; H, 8.82; Si, 15.39. $\text{C}_9\text{H}_{16}\text{O}_2\text{Si}$ calcd.: C, 58.65; H, 8.75; Si, 15.24%.

$\text{CH}_3(-\text{CH}_2(\text{CH}_2)_2\text{CH}_2-)\text{Si}(\text{acac})$: b.p. $78\text{--}80^\circ\text{C}$ (0.2 Torr). Anal. Found: C, 59.50; H, 8.78; Si, 14.43. $\text{C}_{10}\text{H}_{18}\text{O}_2\text{Si}$ calcd.: C, 60.56; H, 9.15; Si, 14.16%.

$\text{CH}_3(-\text{CH}_2(\text{CH}_2)_3\text{CH}_2-)\text{Si}(\text{acac})$: c.p. $67\text{--}68^\circ$, (0.1 Torr). Anal. Found: C, 61.78; H, 9.51; Si, 13.38. $\text{C}_{11}\text{H}_{20}\text{O}_2\text{Si}$ calcd.: C, 62.09; H, 9.45; Si, 13.20%.

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